

Thermophysical Data Inversion: The Limits of Uncertainty¹

I.Herskowitz², and G.G.Kuleshov^{2,3}

¹ Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

² Academic Computing Department, Touro College, New York, NY 10010-4202, U.S.A.

³ To whom correspondence should be addressed. E-mail: genek@touro.edu

ABSTRACT

Both the qualitative and quantitative analyses of the thermophysical data inversion procedure are presented. As a version of the corresponding state approach for obtaining the thermophysical properties of new compounds involved in technology over a wide range of the parameters of state, the inversion procedure means the estimation of the intermolecular potential parameters. These parameters should fit the initial set of experimental thermodynamic or transport properties in the best way, and at the same time, have a capability to predict the other properties that are not yet measured. Such a problem seems to be controversial, especially if one takes into consideration the specific conditions of any particular experiment. The linear approximation of the perturbation theory was developed for the inversion procedure algorithm in order to determine the influence of surface effects, equilibrium admixtures, and their combination that is the selective adsorption to the results of inversion. The small parameter of the theory is determined as the relative deviation between the properties being considered at two different conditions that represent the perturbed and non-perturbed systems. The selective adsorption perturbation parameter is represented as a combination of the above parameters for each component and the perturbed composition of the mixture. These parameters are used to describe the perturbations of both the second virial coefficient and the collision integrals estimated from experimental PVT , and either viscosity, self-diffusivity or heat conductivity data, respectively. It is shown that the influence of adsorption effects leads to systematic errors rather than to random ones. The illustrations and estimations are presented for typical conditions of thermophysical experiments.

KEY WORDS: admixtures, adsorption, collision integral, integrated response, intermolecular potential, inversion procedure, perturbation parameter, second virial coefficient, thermophysical properties, viscosity.

INTRODUCTION

The intermolecular forces determine all the thermodynamic properties of fluids, their kinetic coefficients, and most of the properties of crystals. Because usually characteristics that are some derivative functions of the intermolecular potential, and not the intermolecular forces themselves, have been determined in direct experiments, there is a so-called inversion problem which is a reestablishment of both the shape of potential and its parameters by using experimental data of different kinds. In spite of the well-known difficulties involved in the description of a broad set of thermodynamic and transport properties by using the common universal intermolecular potential function [1], the solution of the inversion problem is still very attractive for at least three reasons. The first reason is the possibility of exploring the nomenclature of properties that can be obtained on the basis of a limited amount of experimental data. The second reason is the possibility of verifying the internal consistency of different properties by using the physically clear criteria. The third reason is the possibility of predicting the behavior of mixtures. Besides these, in the framework of a chosen intermolecular potential function, the parameters of the potential, together with the chemical formula, the temperature of boiling at normal pressure, and the parameters of the critical point, could be considered as a kind of identification for matter.

It is known that it is almost impossible to establish the intermolecular potential over a wide range of distances by using any single property. For example, the branch of attraction is very sensitive to the transport coefficients at low and moderate temperatures, while the width of the potential depends on the second virial coefficient. To establish the intermolecular potential function that allows us to describe both the thermodynamic and the transport properties over a wide range of parameters of state, the above local levels of reliability of different data as well as the response of the results of inversion to the experimental distortions due to the specific conditions of any particular experiment, which are the influence of admixtures and the interaction between the system being considered and the measuring device, should be taken into consideration [2]. Of course, the obtained consistency between experimental and calculated properties is not an evidence of truth of the selected intermolecular potential function. This consistency is a necessary condition rather than a sufficient one to decide if the potential function is an adequate one. The contemporary procedure of inversion of thermodynamic and transport properties [3] allows one to estimate the parameters of the effective (averaged and spherical) intermolecular potentials which demonstrate satisfactory description of most of the properties, and at the same time, allows one to use the discrepancies as a measure of inconsistency of different sets of initial experimental data.

THE INVERSION PROCEDURE AND RANDOM ERRORS

The classical definition of the second virial coefficient is an example of the starting point of the inversion procedure of thermodynamic properties

$$B(T) = -2\pi N_A \int_0^\infty \left\{ \exp\left[-\frac{U(r)}{kT}\right] - 1 \right\} r^2 dr, \quad (1)$$

where N_A is Avogadro number, $U(r)$ is the potential energy of binary interaction, r is the intermolecular distance, k is Boltzmann's constant, and T is the temperature. Developed in [4, 5], the inversion procedure introduces the characteristic distance \tilde{r} , which is determined by the properties being inverted, and in the case of second virial coefficient, by its first derivative

$$\tilde{r} = \left\{ \frac{3 \left[B(T) + T \frac{dB(T)}{dT} \right]}{2\pi N_A} \right\}^{1/3}. \quad (2)$$

The first approximation of the potential function $U(r)$ is used in such an approach as the zero approximation of the inversion function $G_{B(T)}(T^*)$. The iterations utilize the algorithm

$$U^{(n)}(\tilde{r}) = G_{B(T)}^{(n-1)}(T^*)kT, \quad n = 1, 2, 3, \dots \quad (3)$$

where $T^* = kT/\varepsilon$ is the reduced temperature, ε is the depth of the potential, and n is the number of iteration's step. The stabilization of parameters of the spherically symmetrical potentials usually appears on the third step of iteration [5, 6]. It should be emphasized that both the inversion function $G_{B(T)}(T^*)$ and the inversion procedure (3) are not sensitive to the shape of the potential function $U(r)$. Unfortunately, this is not true for “experimental” second virial coefficients, and even less true because the second virial coefficient's first derivative is a factor of the inverse formula (2). The typical values of the second virial coefficient's relative uncertainties $\delta B/B$ are about a few percent [2, 7], while the relative uncertainties of the first derivative $\delta(dB/dT)/(dB/dT)$ are much larger.

The accuracy of the initial data can be higher if, instead of the volumetric second virial coefficient $B(T)$, the acoustic one, $\beta_a(T)$, that is determined by the virial representation of the speed of sound, is used [8]

$$\frac{1}{2} \beta_a(T) = B(T) + (\kappa^0 - 1)T \frac{dB(T)}{dT} + \frac{(\kappa^0 - 1)^2}{2\kappa^0} T^2 \frac{d^2 B(T)}{dT^2}, \quad (4)$$

where $\kappa^0 = C_P^0(T)/C_V^0(T)$ is the ratio of ideal gas specific heat capacities at constant pressure P and at constant volume V , respectively. According to [8], the inaccuracy of the acoustic second virial coefficient $\beta_a(T)$ measurement in contemporary resonators at sound frequencies is about 0.05% (or in the range between 10^{-7} m³/mol for Argon at 273 K and 10^{-6} m³/mol for C₅H₁₂ at its normal boiling point). The method of recalculation of the acoustic second virial coefficient into the volumetric one, which has been described in detail in [8], allows one to eliminate the numerical differentiation and as a result, makes it possible to obtain the depth of the potential (ε/k) for spherically symmetrical molecules within ± 1 K of error. However, such an approach can be limited due to the absence of reliable specific heat capacity data.

The kinetic coefficients of the spherically symmetrical molecules are determined by a set of collision integrals $\Omega^{(l,s)}(T)$ [3]

$$\Omega^{(l,s)}(T) = \frac{1}{(s+1)!(kT)^{s+2}} \int_0^\infty Q^{(l)}(E) E^{s+1} \exp\left(-\frac{E}{kT}\right) dE, \quad (5)$$

where

$$Q^{(l)}(E) = 2\pi \left[1 - \frac{1 + (-1)^l}{2(1+l)} \right] \int_0^\infty (1 - \cos^l \chi) b db \quad (6)$$

are the cross sections, and

$$\chi(b, E) = \pi - 2b \int_{r_c}^\infty \left[1 - \frac{b^2}{r^2} - \frac{U(r)}{E} \right]^{-\frac{1}{2}} \frac{dr}{r^2} \quad (7)$$

are the angles of scattering, with r_c representing the shortest distance at the collision, b representing the sighting parameter, and E representing the relative kinetic energy of molecules. For example, the viscosity of dilute gas can be expressed as

$$\eta_0(T) = \frac{5}{16} \frac{(\pi m k T)^{\frac{1}{2}}}{\Omega^{(2,2)}(T)} f_\eta, \quad (8)$$

where m is a mass of a molecule, and f_η is the correction factor that is not sensitive to the shape of pair potential and which is equal to 1 in the first approximation of the kinetic theory. The coefficient of self-diffusivity of the dilute gas can be represented via the collision integral $\Omega^{(1,1)}(T)$

$$D(T) \approx \frac{(T^3 / M)^{1/2}}{P \Omega^{(1,1)}(T)}, \quad (9)$$

and so on. The characteristic distance \tilde{r} of kinetic coefficients' inversion is

$$\tilde{r} = [\Omega^{(l,s)}(T^*)]^{1/2}. \quad (10)$$

The functions $G_\Omega(T^*)$ that are necessary to complete the inversion iteration process similarly to (3) can be found in [9] within a wide range of reduced temperatures T^* .

The described method can easily be expanded to cover the inversion procedure of anisotropic molecules' thermophysical properties, as well. For example, the second virial coefficient, instead of (1), can be represented as

$$\bar{B}(T) = -\frac{N_A}{4} \int_0^\infty r^2 dr \int_{-1}^1 d(\cos\theta_1) \int_{-1}^1 d(\cos\theta_2) \int_0^\pi f_{12} d\varphi_{12}, \quad (11)$$

where θ_1 , θ_2 , and $\varphi_{12} = \varphi_1 - \varphi_2$ are angles of orientation, and f_{12} is Mayer's anisotropic function

$$f_{12} = \exp[-U(r, \theta_1, \theta_2, \varphi_{12}) / kT]. \quad (12)$$

The similar averaging of the collision integrals over all the orientations θ can be done in the same way

$$\bar{\Omega}^{(l,s)}(T) = \langle \Omega_\theta(T) \rangle = \frac{1}{2} \int_{-1}^1 \Omega_\theta(T) d(\cos\theta). \quad (13)$$

In such a case, the iteration process converges more slowly [10], whereas the obtained effective potential averaged over all the orientations still satisfactorily describes

individual properties of molecules having relatively low anisotropy ($L/\sigma < 0.5$ where L is the length of a linear molecule and σ is the equilibrium distance between two molecules) [11]. The problem appears when one attempts to describe two different properties using one common set of potential parameters. Even for noble gases, the problem of prediction of both the thermodynamic and the transport properties using a unique pair of parameters has not yet been solved successfully. Table 1 shows some typical results [12 -14] for Argon.

Table 1. Parameters of Lennard-Jones (12-6) potential of Argon estimated by inversion of different thermophysical properties.

Property (Properties)	ϵ /k , K	$\sigma \cdot 10^{10}$, m	Reference
Zero Approximation (Start Up Values)	119.80	3.4050	[12]
Second Virial Coefficient + Adiabatic Throttle-Effect	124.20	3.8279	[13]
Second Virial Coefficient +Viscosity	123.68	3.8124	[13]
Heat Conductivity	135.0	3.346	[14]

Table 2 illustrates the sensitivity of the inversion procedure of simulated “experimental” data to the range of temperatures and to the nomenclature of the properties [13]. The simulated “experimental” data was obtained by the calculation (at $\epsilon /k = 152.8$ K, $r_m = 0.36744$ nm, and $\gamma = 3$) of the second virial coefficient and adiabatic throttle-effect values distorted randomly with amplitudes of $|\Delta B(T)| = 0.53 \cdot 10^{-6}$ m³/mol, and $|\Delta \mu| = 0.073$ K/MPa, respectively. As it follows from Table 2, the satisfactory description (within the range of the forced errors) of both the above properties is difficult if one used only the second virial coefficient data, even over a wide range of temperatures. At the same time, the adiabatic throttle-effect data allows one to estimate parameters that are capable of predicting both properties with an average deviation that is less than the initial distortion. The most important thing to note is that the inversion procedure converges very well if

the range of temperatures is wide enough to represent the wide range of corresponding characteristic distances.

Table 2. Parameters of the potential 11-6-8 of Argon estimated by inversion of second virial coefficient $B(T)$ and adiabatic throttle-effect μ .

Temperature range, K		Potential parameters			Average amplitude of deviations	
$B(T)$	μ	ε/k , K	r_m , nm	γ	$ \Delta B(T) \cdot 10^6 $, m^3/mol	$ \Delta \mu $, K/MPa
80 - 225		143.9	0.37767	2.7	1.28	0.34
80 - 1,000		151.4	0.36770	2.8	0.60	0.13
	80 - 400	153.8	0.36510	2.9	0.41	0.03
80 - 225	80 - 400	151.7	0.36847	2.9	0.33	0.07
80 - 1,000	80 - 400	152.5	0.36739	2.9	0.29	0.05

Table 3. Comparison of different potentials used to describe the heat conductivity. (LJ means Lennard-Jones, and BFW means Barker-Fisher-Watts.)

Gas	Temperatures, K	Potential*	Parameters		Deviations, %	
			ε/k , K	σ , nm	$\langle \Delta \lambda \rangle$	$(\Delta \lambda)_{\max}$
Ne	400 - 2,500	LJ 12-6	43.0	0.2724	0.9	1.6
		11-6-8	43.4	0.2710	0.9	1.8
		exp-6	43.0	0.3030	1.0	2.0
Ar	400 - 2,500	LJ 12-6	135.0	0.3345	0.4	1.6
		BFW	142.1	0.3761	0.3	1.4
		LJ 12-7	152.0	0.3304	0.6	1.0
		11-6-8	152.8	0.3297	0.5	1.3
Kr	400 - 2,500	LJ 12-6	193.0	0.3566	1.3	2.9
		11-6-8	215.8	0.3513	1.8	4.0
Xe	800 - 2,000	LJ 12-6	256.0	0.3923	1.4	1.8
		11-6-8	295.0	0.3841	0.4	0.6

It should be emphasized that the different potentials have approximately equal capabilities of predicting any single property. For example, Table 3 summarizes the results of heat conductivity coefficients of noble gases, which have been calculated using seven different potentials [14].

The above numerical results testify that the most difficult step in the inversion of thermophysical properties is the usage of second virial coefficient data at relatively low temperatures (Table 2). Another factor that affects the inversion procedure is the temperature range of initial data, because the shorter the range of temperatures is, the shorter the range of characteristic distances \tilde{r} is, and as the result, the less precise the estimate of the parameters will be.

THE EXTERNAL INFLUENCES AND SYSTEMATIC ERRORS

The analysis of second virial coefficient data [2, 6] shows that there are sufficient discrepancies between virial coefficients determined separately at high and low pressures. For some compounds, there are anomalies of behavior of isotherms in Keyes' diagram at relatively high molar volumes. The possible reason for such anomalies and discrepancies may be the adsorption processes of gases being investigated on the surface of the experimental cell, the influence of admixtures, and cross effects that are caused by the selective adsorption of either solvent or admixture. The first estimates of the above effects were completed [6] using de Boer's concept of physical adsorption [15]. Later, these estimates were confirmed experimentally by utilizing Barnett's method of measurement of second virial coefficient [7] and the constant volume cell method [16].

To represent the perturbed pressure P^* as a function of perturbed volume $V^* = V(1+t)$, the standard virial equation of state should be rewritten as

$$P^*(V^*, T) = \frac{RT}{V^*} \left[1 + \frac{B_2(T)}{V^*} + \dots \right] = \frac{RT}{V} \left[1 + \frac{B_2^*(T)}{V} + \dots \right]. \quad (14)$$

where $B_2(T)$ and $B_2^*(T)$ are non-perturbed and perturbed second virial coefficients, respectively. In the first approximation of the thermodynamic theory of perturbations, the relationship between a second virial coefficient $B_2^*(T)$ perturbed by auto-adsorption effects and a non-perturbed one $B_2(T)$ might be expressed as

$$B_2^*(T) = \frac{B_2(T)}{(1+t)^2} - \frac{t}{t+1} V_0, \quad (15)$$

where $0 < t = N_a/N < 1$. Here, N_a and N are the number of adsorbed molecules and the total number of molecules in the system, respectively. For a spherical cell of volume V_0 , when Q_a is measured in J/mol, and M is the molar mass of the molecules,

$$t = 1.15 \cdot 10^{-13} \frac{\sqrt{T/M}}{V_0^{1/3}} \exp\left(\frac{Q_a}{RT}\right) \quad (16)$$

is the perturbation parameter which depends on the temperature T , the heat of adsorption Q_a , and the volume V_0 of the experimental cell. The first term in (15) represents the clockwise turn around the zero value (at Boyle's temperature T_B) of temperature dependence of the second virial coefficient, whereas the second term represents the shift of the above dependence graph along the temperature axis (or T_B change).

Similarly, the response of the viscosity to the adsorption perturbation can be estimated via perturbation of molar volume that determines the first density correction $\alpha(T)$ of the viscosity

$$\eta(T) = \eta_0(T) \left[1 + \frac{\alpha(T)}{V(1+t)} + \dots \right], \quad (17)$$

where $\eta_0(T)$ is defined by (8).

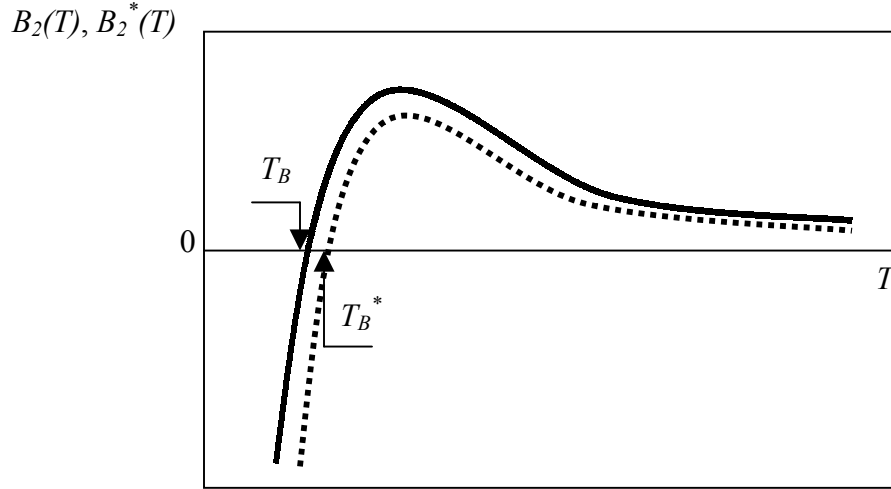


Figure 1. The comparison of the non-perturbed $B_2(T)$ (solid line) and $B_2^*(T)$ perturbed by adsorption effects (dashed line) second virial coefficients.

The numerical estimates (Table 4 and 5) of the Lennard-Jones 12-6 potential parameters' response to the adsorption perturbation have been completed for Xenon and Nitrogen at the assumption that $V_0 = 10^{-6} \text{ m}^3$ and Q_a is equal to 29 kJ/mol and 17 kJ/mol , respectively. The tabulated data of the reduced second virial coefficient $B_2^*(T^*)$ and the collision integral $\Omega^{(l,s)*}(T^*)$, as well as the initial values of the parameters $(\epsilon/k)_0$ and σ_0 , were taken from [17]. The inversion procedure was applied repeatedly to different values of (ϵ/k) , and then the averaged deviation of three properties (second virial coefficient $B_2(T)$, self-diffusivity $D(T)$, and viscosity $\eta(T)$) were compared in order to find the set of parameters which fit the calculated values in the best way.

Table 4. Response of the Lennard-Jones 12-6 parameters of Xe to the adsorption perturbations estimated by inversion of second virial coefficient, self-diffusivity, and viscosity data with zero approximation of $(\epsilon/k)_0 = 267.0$ K and $\sigma_0 = 0.3950$ nm.

$B_2(T)$			$D(T)$			$\eta(T)$		
(ϵ/k), K	σ , nm	$\langle \delta \rangle$, %	(ϵ/k), K	σ , nm	$\langle \delta \rangle$, %	(ϵ/k), K	σ , nm	$\langle \delta \rangle$, %
265.0	0.3955	1.37	220	0.4076	0.91	240	0.4002	0.66
265.5	0.3954	0.33	230	0.4045	0.39	250	0.3981	0.19
266.0	0.3952	0.65	240	0.4017	0.08	254	0.3974	0.01
267.0	0.3950	2.77	250	0.3990	0.25	260	0.3962	0.22
268.0	0.3948	5.33	260	0.3966	0.46	265	0.3955	0.48
$(\epsilon/k)^* = 265.6$ K			$(\epsilon/k)^* = 238$ K			$(\epsilon/k)^* = 254.5$ K		
$\sigma^* = 0.3954$ nm			$\sigma^* = 0.4020$ nm			$\sigma^* = 0.3973$ nm		

Table 5. Response of the Lennard-Jones 12-6 parameters of N₂ to the adsorption perturbations estimated by inversion of second virial coefficient, self-diffusivity, and viscosity data with zero approximation of $(\epsilon/k)_0 = 95.05$ K and $\sigma_0 = 0.3698$ nm.

$B_2(T)$			$D(T)$			$\eta(T)$		
(ϵ/k), K	σ , nm	$\langle \delta \rangle$, %	(ϵ/k), K	σ , nm	$\langle \delta \rangle$, %	(ϵ/k), K	σ , nm	$\langle \delta \rangle$, %
93.00	0.3713	2.78	70.00	0.3890	2.29	60.0	0.3943	0.49
93.70	0.3708	1.02	75.00	0.3840	1.89	65.0	0.3893	0.18
94.03	0.3705	0.44	80.00	0.3800	1.68	70.0	0.3850	0.14
95.05	0.3703	0.16	90.00	0.3730	1.61	75.0	0.3812	0.08
95.05	0.3698	2.25	95.05	0.3698	1.71	80.0	0.3788	0.48
96.05	0.3694	4.97	100.00	0.3670	1.99	93.0	0.3708	1.56
$(\epsilon/k)^* = 94.1$ K			$(\epsilon/k)^* = 86.0$ K			$(\epsilon/k)^* = 74.0$ K		
$\sigma^* = 0.3704$ nm			$\sigma^* = 0.3760$ nm			$\sigma^* = 0.3816$ nm		

The adsorption effects in mixtures involving $k - 1$ admixtures are characterized by the parameter of adsorption-admixture perturbation t_m

$$t_m = 1.15 \cdot 10^{-13} \frac{\sqrt{T}}{V_0^{1/3}} \sum_{i=1}^k \left[\frac{x_i^*}{\sqrt{M_i}} \exp\left(\frac{Q_{ai}}{RT}\right) \right], \quad (18)$$

similar to (16), where x_i^* is the perturbed composition of the mixture as the result of selective adsorption which might be determined by iteration procedure described in [18]. The presence of admixtures can either increase or decrease the adsorption perturbation. For example, addition of 0.01% of Xenon to Helium increases t_m up to 300 times [2]. Much more interesting is to find out the fraction of a certain admixture that affects the potential parameters the same way as the adsorption of a solvent. To do that let us use so-called “single liquid” approximation

$$\sigma_m = x_1^2 \sigma_{11} + 2x_1 x_2 \sigma_{12} + x_2^2 \sigma_{22} \quad (19)$$

and

$$(\varepsilon/k)_m = x_1^2 (\varepsilon/k)_{11} + 2x_1 x_2 (\varepsilon/k)_{12} + x_2^2 (\varepsilon/k)_{22}, \quad (20)$$

where indexes m , 1 and 2 denote the mixture, the solvent and the admixture; x_1 and x_2 are mole fractions; and σ_{12} and $(\varepsilon/k)_{12}$ should satisfy the combinatory rules

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}), \quad (21)$$

and

$$(\varepsilon/k)_{12} = \sqrt{(\varepsilon/k)_{11}(\varepsilon/k)_{22}}. \quad (22)$$

In such an approximation, the second virial coefficient of the solvent could be estimated by the expression

$$B_{11}(T) = \frac{1}{x_1^{*2}} \left[(1 + t_m)^2 B_{\text{exp}}(T) - 2x_1^* x_2^* B_{12}(T) - x_2^{*2} B_{22}(T) + t_m (1 + t_m) V_0 \right], \quad (23)$$

where $B_{\text{exp}}(T)$ is the “experimental” value of the second virial coefficient, $B_{11}(T)$ and $B_{22}(T)$ represent the solvent and the admixture, $B_{12}(T)$ is estimated by using (21) – (22), and the composition of the mixture $\{x_1^*, x_2^* = 1 - x_1^*\}$ is normalized by 1. At $x_1^* \rightarrow 1$, the equation (23) converts into the equation (15) when (16) converts into (18). The expression (23) allows us to compare the adsorption effect in pure solvent with the admixture effect due to selective adsorption. In other words, it allows one to find out the composition of the mixture that leads to the same perturbation of the second virial coefficient as the adsorption effect in pure solvent. Table 6 illustrates the response of the cross second virial coefficient $B_{12}^*(T)$ of Kr – SF₆ mixture to the adsorption and admixture perturbations [2].

Table 6. The cross second virial coefficient B_{12}^* (cm³/mol) of Kr – SF₆ equimolar mixture at 273 K as a function of selective adsorption of compounds. (Here, $\Delta x_1 = x^* - 0.5$ is the composition change).

t_m	$\Delta x_1 = x^* - 0.5$				
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	$10^{-\infty}$
10^{-1}	-219.3	-168.7	-163.7	-163.2	-163.1
10^{-2}	-188.2	-138.8	-133.9	-133.4	-133.3
10^{-3}	-185.1	-135.8	-130.9	-130.4	-130.3
10^{-4}	-184.8	-135.6	-130.6	-130.1	-130.0
$10^{-\infty}$	-184.8	-135.5	-130.6	-130.1	-130.0

The right column of the above table shows the expected changes of the second virial coefficient only the result of adsorption effects whereas the last row of data represents only the impurities effect. It is visible from the above table that adsorption processes and impurities affect the second virial coefficient in two opposite directions; therefore, the combined influence of both effects can be mutually eliminated. The situation that arises in any specific experiment depends on the heat of adsorption of compounds and the temperature. The lower the temperature is, the more developed adsorption is, and when parameters of state approach the gas – liquid coexistence curve, capillary condensation may appear [19]. In such a case, the experimental data cannot be used at all for the inversion procedure. A similar problem has been discussed in [20], where the characteristic distance r obtained from viscosity data eventually becomes negative at low temperatures.

CONCLUSIONS

The first conclusion from the developed analysis is that the thermophysical data inversion procedure is much more sensitive to systematic experimental errors than to nonsystematic random ones. Consequently, accurate data over wide temperature and density ranges, together with impurities and heat of adsorption identification, are needed to determine reliable values of intermolecular potential parameters. The second conclusion is that the impurities affect the inversion procedure in a definite but still random way, whereas the adsorption processes affect the inversion in a systematic asymmetrical way. The presented concept allows one to discuss the external influences

much more definitely than by using the regular approach of random deviation statistical analysis.

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